

HYDRODESULFURIZATION OF DIBENZOTHIOPHENE OVER Mo-BASED DISPERSED CATALYSTS

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The hydrodesulfurization (HDS), hydrocracking (HC) activity and selectivity of several Mo, Co and Fe-based catalyst precursors have been examined in model compound reactions of dibenzothiophene (DBT). Reactions were carried out at 400 °C with 6.9 MPa of H₂ for 30 min. A metal loading of 0.5 mol % (based on DBT) in tridecane as solvent resulted in a low conversion rate and only hydrogenation products. Even the addition of sulfur to the catalyst in a 4:1 molar ratio only led to a minor increase in conversion and HDS. However, a change in the molar ratio of solvent to model compound from 1:1 to 19:1 and a metal loading of 36.16 mol % lead to a dramatic increase in conversion, HDS, and HC. Furthermore, the use of higher boiling point solvents such as hexadecane and octadecane had a beneficial effect on both HDS and HC. The addition of sulfur in a 6:1 ratio of S:metal to the higher-metal-loaded runs had varying effects that were dependent upon the catalyst used.

Keywords: Model reactions, hydrocracking, dispersed catalysts.

INTRODUCTION

The objective of this work is to examine the hydrodesulfurization activity of dispersed catalysts under coal liquefaction conditions. Most coal hydroliquefaction reactions (1) are performed at temperatures in excess of 400 °C and 6.9 MPa H₂ for at least 30 min. These severe conditions are required to break the heteroatom and alkyl bridges that connect the aromatic species. Different metal catalysts, in particular molybdenum (2), have been known to be effective in coal liquefaction reactions. The complex nature of coal renders the study of reactions of a specific coal molecule impossible and thus obscures the effectiveness of a particular catalyst. Some catalysts are particularly effective for HC, others better for desulfurization and denitrogenation. Coals with a high heteroatom (sulfur) content, are of concern in combustion processes and pose an environmental risk. Multistage liquefaction is expected to improve selectivity for specific reactions, such as desulfurization, to meet current refining regulations. The model compound chosen for the examination of the hydrodesulfurization was dibenzothiophene (DBT). The catalysts chosen for this study were, ammonium tetrathiomolybdate (ATTM), molybdenum hexacarbonyl, MoCl₃, Co₂(CO)₈, Fe(CO)₅ with and without added sulfur, and the thiocubane type bimetallic catalyst precursor Cp₂Co₂Mo₂(CO)₂S₄ [MoCo-TC2].

EXPERIMENTAL

Materials

The model compound dibenzothiophene (98% purity) and the solvents tridecane, heptadecane, and octadecane (all 99% purity) were obtained from Aldrich; Mo(CO)₆ obtained from Johnson Matthey, ATTM and MoCl₃ from Aldrich, Fe(CO)₅ and Co₂(CO)₈ from Strem. The thiocubane type complex Cp₂Co₂Mo₂(CO)₂S₄ [MoCo-TC2] was prepared according to the method of Brunner and Wachter (3). Elemental sulfur was obtained from J. T. Baker Chemical Co. All chemicals and precursors were used as received.

Conditions and Procedures

Experimental runs with the model compound DBT were carried out in 33 mL reactors using ca. 1 g of DBT and various solvent to model compound ratios at 400 °C for 30 min, in the presence of catalyst precursors (0.5-36.16 mol % metal based on DBT). When sulfur was added to a S-free precursor, the S:metal atomic ratio was 4:1, unless otherwise mentioned. For those experiments involving water, the above procedure was used with the addition of water in a H₂O:DBT molar ratio of 10:1. The remainder of experiments involved a metal loading of 36.16 mol % (with respect to DBT). In another set of experiments, catalysts were added to a reaction solution consisting of 1% DBT and 99% solvent. Sulfur was added to S-free precursors in a S:metal ratio of 6:1. The reaction temperature primarily employed was 400 °C, except for those experiments involving water in which case 350 °C was used. The reactor was purged three times with H₂ and then pressurized with 6.9 MPa H₂ at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in cold water. The liquid contents were washed with 15 ml CH₂Cl₂ through a low speed filter paper for qualitative and quantitative GC analysis of the filtrate. Most runs were carried out twice to confirm reproducibility.

Analysis

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50 % phenyl-50 % methylpolysiloxane with a coating film thickness of 0.25 µm. For quantification, a HP 5890 II GC with flame ionization detector and the same type of column (DB-17) was used. Both GC and GC-MS were temperature programmed from 40 to 260 °C at a heating rate of 4 °C/min. The response

factors for 5 of the products were determined using pure compounds. Conversion was determined by the amount of unreacted DBT recovered after the reaction. Yields of products were calculated as molar percentage based on DBT reactant. More experimental details may be found elsewhere (4).

RESULTS AND DISCUSSION

Initially, DBT hydrosulfurization tests were performed at 400 °C over ATTM and $\text{Mo}(\text{CO})_6$ using a metal loading of 0.5 mol % with and without added sulfur in a S:metal ratio of 4:1. Table 1 and Figure 1 show the results of these runs. At such a low loading level, both precursors displayed only moderate catalytic activity. However, when S was added to the S-free precursor, conversion increased significantly. The HDS activity of $\text{Mo}(\text{CO})_6$ was improved when a higher metal loading of 5 mol % Mo (with respect to DBT) was used. This suggests that a much higher metal concentration would be needed to completely convert and hydrosulfurize DBT under the conditions used.

To study the impact of different metal concentrations on DBT conversion, a much higher metal loading, 36 mol % with respect to DBT, was also used in examining the performance of various catalyst precursors. Table 2 and Figure 2 give the results with $\text{Mo}(\text{CO})_6$ and ATTM. The reactions with $\text{Mo}(\text{CO})_6$ and ATTM were performed using tridecane and octadecane as solvents. The liquid products identified from these reactions were biphenyl (BP), tetrahydrodibenzothiophene (TH-DBT), cyclohexylbenzene (CHB), bicyclohexyl (BCH), and benzene (BNZ). It should be noted that there are un-identified products, which are not included in Table 2. One of them has MW of 166. It could be cyclopentylmethylcyclohexane, but this needs to be confirmed. For the runs with $\text{Mo}(\text{CO})_6$, increase in Mo loading from 0.5, to 5 and to 36 mol % with respect to DBT increased the DBT conversion with tridecane solvent from 5.5 to 26.2 to 53.4 mol %. Adding sulfur further increased the catalytic activity for DBT conversion. A comparison of the results for ATTM with different metal loadings (Tables 1 and 2) showed a substantial increase of DBT conversion and HDS degree (as expressed by the sum of HDS products). Reactions with ATTM at 0.5 mol % metal loading gave DBT conversions up to 21.2 %, with only HDS and partial hydrogenation products (Table 1). A great impact on conversion, HDS, and product distribution could be found in model reactions with ATTM at 36 mol % metal loading (Table 2). The products include not only HDS products such as BP and CHB, but also hydrocracking products such as benzene. Highest conversions were achieved using octadecane as a (high boiling) solvent in combination with added S.

As shown in Table 3 and Figure 3, the precursors used in the high metal-loading runs also included were MoCl_3 , $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$ with and without sulfur, and the bimetallic catalyst MoCo-TC2 , in addition to ATTM and $\text{Mo}(\text{CO})_6$. Again, most of these catalysts were run with tridecane and octadecane as solvents, and in some cases heptadecane was also used. The ratio of S:metal ratio employed was 6:1. As seen in Tables 2 and 3 the use of high metal concentrations dramatically increased conversion and HDS.

From the DBT conversion data in Tables 2 and 3, $\text{Mo}(\text{CO})_6$ appears to be the most active precursor and showed highest selectivity. The reactions of $\text{Mo}(\text{CO})_6$ lead to 50.8 % HDS and a conversion of 53.4 % using tridecane as a solvent. These percentages increase when tridecane was replaced with octadecane. The use of octadecane increased HDS (50.8 % to 80.0 %) and increased conversion (53.4 % to 75.8 %). When sulfur was added in a 6:1 S:metal ratio the results for tridecane were 41.2 % HDS and 100 % conversion, and for octadecane 43.2 % for HDS. The influence of S was studied in a set of experiments using a 2:1 and a 6:1 S:metal ratio. Both runs were conducted with heptadecane as a solvent. Sulfur addition resulted in high HDS yield and complete conversion but different product distribution. In the latter reaction cyclohexylbenzene (CHB), bicyclo-hexyl (BCH), and benzene (BNZ) accounted for most of the products. This effect is also present when using a higher boiling point solvent. CHB, BCH, and BNZ accounted for 100 % of the products of the run with $\text{Mo}(\text{CO})_6$, added sulfur and octadecane, as compared to runs, using heptadecane and tridecane under the same conditions. These results indicate that oil-soluble $\text{Mo}(\text{CO})_6$ may be used for HDS reactions. Curtis (5) demonstrated that catalytic desulfurization can be achieved in high yields by using molybdenum naphthenate, which is another oil-soluble precursor.

The 36 mol % metal loaded samples of ATTM easily outperformed the 0.5 mol % samples. The total yields of HDS products with ATTM, however, are lower than those with $\text{Mo}(\text{CO})_6$ without sulfur and much lower than those with $\text{Mo}(\text{CO})_6$ with sulfur. This is surprising, considering that ATTM has a S:metal ratio of 4:1 compared to no precursor sulfur for $\text{Mo}(\text{CO})_6$, and ATTM was shown to be more effective than $\text{Mo}(\text{CO})_6$ in our coal liquefaction experiments. The performance of ATTM, like $\text{Mo}(\text{CO})_6$, was also affected by the solvent used. The use of octadecane increased HDS from 24.8 % to 36.0 % and conversion from 40.4 % to 74.6 %. The product distribution also changed. An increase in HDS and hydrogenation products, such as BP, TH-DBT, and CHB could also be observed.

MoCl_3 gave about the same results as ATTM, in terms of HDS and conversion in both solvents (Table 3). However, the addition of sulfur to MoCl_3 resulted in a considerable decrease in both HDS and conversion. The use of $\text{Co}_2(\text{CO})_8$ in octadecane gave relatively low conversion, which indicates that the material from $\text{Co}_2(\text{CO})_8$ itself is less active for DBT conversion under the conditions employed. Although sulfur was not used, it could possibly increase the activity of $\text{Co}_2(\text{CO})_8$ as it did for $\text{Mo}(\text{CO})_6$. The use of the bimetallic catalyst MoCo-TC2 did not give an improvement over the individual Co or Mo catalysts. In fact, the results were almost identical to runs using $\text{Co}_2(\text{CO})_8$. It should be mentioned that the above results apply only to the HDS using in situ generated catalyst from MoCo-TC2 . The last precursor used was $\text{Fe}(\text{CO})_5$, with and without

added sulfur. They were the least active precursors, among all those tested with octadecane solvent. This is probably due to the low hydrogenation activity and HDS activity of the Fe catalysts. An additional reason for the lack of activity of $\text{Fe}(\text{CO})_5$ is the preferred formation of less reactive iron carbides (6) and iron oxides over iron sulfides.

$\text{Mo}(\text{CO})_6$ and ATTM were also used at 0.5 mol % metal loading in reactions at 350 °C involving water. Previous work by Song (7) demonstrated the promoting effect of water addition in coal liquefaction experiments under low severity reaction conditions. Water was added in a H_2O :DBT molar ratio of 10:1. The results obtained so far were not conclusive. The product recovery was poor with CH_2Cl_2 as the solvent for recovering products from the reactions with H_2O . It is considered that replacing CH_2Cl_2 with acetone as the wash solvent may improve the product recovery.

CONCLUSIONS

Dibenzothiophene appeared to be relatively stable under thermal conditions and reacts only with very active catalysts and high metal loadings to form hydrodesulfurized products. $\text{Mo}(\text{CO})_6$ (36 mol % metal loading) with added sulfur in a S:metal ratio of 6:1 and octadecane as solvent was found to be the most active catalyst yielding 100% HDS and conversion at 400 °C. ATTM and MoCl_3 appear to be less active for DBT HDS under similar conditions. The other catalyst precursors, $\text{Co}_2(\text{CO})_8$, MoCo-TC_2 , and $\text{Fe}(\text{CO})_5$, showed only moderate activity. The use of high boiling solvent seems to be beneficial to HDS, conversion, and the formation of hydrogenation products.

In model reactions using ATTM and $\text{Mo}(\text{CO})_6$ (0.5 mol % metal loading) with and without added sulfur only low catalytic activity could be observed. The product distribution in runs using a metal loading of 0.5 mol % revealed only hydrogenation products.

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Table 1. Catalytic Hydrodesulfurization of Dibenzothiophene with Mo-Based Precursors [0.5 - 5 mol % metal loading].

Experiment #	BLDA3/4	BLDA5	BLDM5/6	BLDM12	BLDM10/11	BLDMS1/2	BLDMS5
Catalyst Precursor	ATTM ^a	ATTM ^{b, #}	Mo(CO) ₆ ^a	Mo(CO) ₆ ^b	Mo(CO) ₆ [5 mol %] ^a	Mo(CO) ₆ + S ^a	Mo(CO) ₆ + S ^b
Products [mol %] ^c							
TH-DBT	5.4	4.6	0.4	0.8	2.5	7.7	8.0
BP	2.5	2.0	1.9	3.0	5.6	3.9	4.3
CHB	1.2	0.9	0	0.1	0.4	1.8	2.1
BCH	0		0	0	0	0	0
BNZ	0		0	0	0	0	0
HDS products	3.7	2.9	1.9	3.1	6.0	5.7	6.3
Conversion [wt %]	21.2	7.4	5.5	17.1	26.2	38.2	17.8

Solvent: ^atridecane, ^boctadecane. ^c biphenyl (BP), tetrahydro-dibenzothiophene (TH-DBT), cyclohexylbenzene (CHB), bicyclohexyl (BCH), and benzene (BNZ).

Needs to be re-run to check the reproducibility.

Table 2. Catalytic Hydrodesulfurization of Dibenzothiophene with Mo-Based Precursors [36 mol % metal loading].

Experiment #	BCDA5	BCDA4	BCDM1/2	BCDM6/5	BCDMS1/2	BCDMS5/6	BCDMS7	BCDMS8
Catalyst Precursor	ATTM ^a	ATTM ^b	Mo(CO) ₆ ^a	Mo(CO) ₆ ^b	Mo(CO) ₆ +S ^a	Mo(CO) ₆ + S [2:1] ^c	Mo(CO) ₆ + S [6:1] ^c	Mo(CO) ₆ + S [6:1] ^b
Products [mol %]								
TH-DBT	3.3	4.7	2.1	2.1	5.5	0	0	0
BP	6.4	11.4	39.1	48.3	26.6	9.9	2.6	0
CHB	11.7	17.7	8.5	14.1	41.7	20.7	23.0	19.1
BCH	3.2	3.2	0	14.6	0	2.5	4.7	11.0
BNZ	3.5	3.7	3.2	3.0	25.7	15.8	10.9	13.8
HDS	24.8	36	50.8	80.0	94.0	48.9	41.2	43.9
Conversion [wt %]	40.4	74.6	53.4	75.8	70.5	99.1	100.0	100.0

Solvent: ^atridecane, ^boctadecane, ^cheptadecane.

Table 3. Catalytic Hydrodesulfurization of Dibenzothiophene with Mo-Based Precursors [36 mol % metal loading].

Experiment #	BCDT3	BCDT2	BCDTS3	BCDTS2	BCDC1	BCDC2	BCDMC1	BCDF1	BCDFS1
Catalyst Precursor	MoCl ₃ ^a	MoCl ₃ ^b	MoCl ₃ +S ^a	MoCl ₃ +S ^b	Co ₂ (CO) ₈ a, #	Co ₂ (CO) ₈ b	MoCo- TC ₂ ^b	Fe(CO) ₅ ^b	Fe(CO) ₅ +S ^b
Products [mol %]									
TH-DBT	0	6.9	4.1	4.5	0	0	2.5	0	0
BP	33.3	42.5	11.3	12.0	0	5.6	7.0	4.4	4.5
CHB	0	2.3	2.8	11.5	0	13.1	11.5	10.0	15.1
BCH	0	0	0	3.8	0	13.1	0	0	0
BNZ	7.0	13.2	7.4	5.0	0	0	0	0	0
HDS	40.3	58.0	21.5	32.3	0	31.8	18.5	14.4	19.6
Conversion [wt %]	52.6	67.3	45.2	48.4	0	19.6	16.3	5.0	8.5

Solvent: ^atridecane, ^boctadecane. # Needs to be re-run to check the reproducibility.

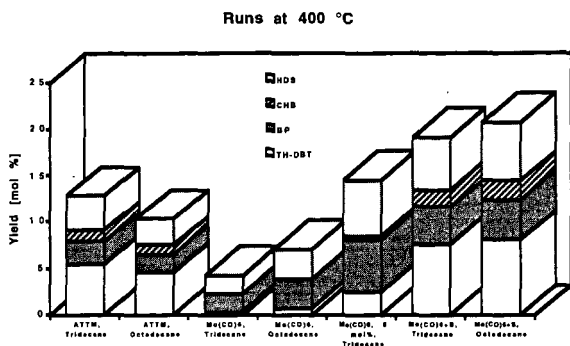


Figure 1. Catalytic Hydrosulfurization of Dibenzothiophene with Mo-Based Precursors [0.5 - 5 mol % metal loading].

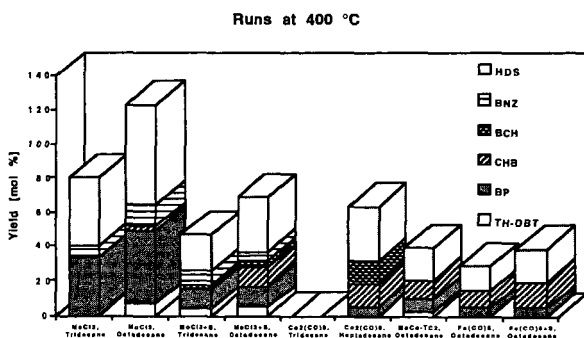


Figure 2. Catalytic Hydrosulfurization of Dibenzothiophene with Mo-Based Precursors [36.16 mol % metal loading].

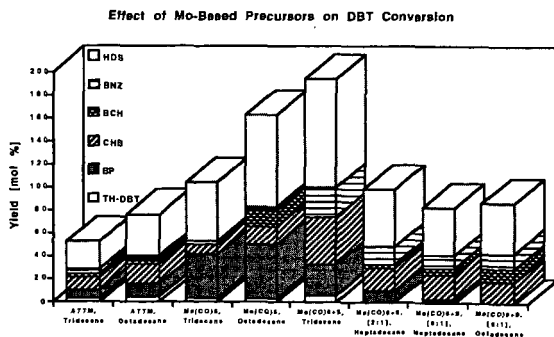


Figure 3. Catalytic Hydrosulfurization of Dibenzothiophene with Mo-Based Precursors [36 mol % metal loading].